

Wisconsin Highway Research Program

Laboratory Study of High Performance Curing Compounds for Concrete Pavement

Wisconsin Highway Research Program
LIMITED USE DOCUMENT

This proposal is for use of the recipient in selection of a research agency to conduct work under the Wisconsin Highway Research Program. If the proposal is unsuccessful, it should be destroyed. Proposals are regarded as fully privileged, and dissemination of the information included therein must be approved by WHRP.

**University of Wisconsin-Madison
March, 2010**

Summary Page

Project Title: Laboratory Study of High Performance Curing Compounds for Concrete Pavement

Proposing Agency: University of Wisconsin-Madison Dept. of Civil and Environmental
Engineering 1415 Engineering Drive University of Wisconsin-Madison
Madison, WI 53706

Person Submitting the Proposal: Steven M. Cramer Professor
Director of Structures and Materials Testing Laboratory, Univ. of
Wisconsin-Madison.

Proposal Written By: Steven M. Cramer
Jessica M. Sanfilippo

Proposal Date: 03/03/2010

Principal Investigator: Steven M. Cramer, PhD, PE
Professor and Director of Structures and Materials Testing Laboratory,
Univ. of Wisconsin-Madison.
2620 Engineering Hall, 1415 Engineering Dr, Madison, WI 53706. Phone:
608-265-2001 Email: cramer@engr.wisc.edu

Co-Principal Investigator: Marc A. Anderson, PhD
Professor and Chair of Environ. Chem. & Tech. Program,
Univ. of Wisconsin-Madison.
660 N. Park St., Madison, WI, 53706
Phone: 608-262-2674 Email: nanopor@wisc.edu

Administrative Officer: Tamara C. Kuhn Martin
Title Admin. Program Spec. College of Engineering
2630 Engineering Hall, 1415 Engineering Dr, Madison, WI 53706 Phone
(608) 265-0504 Email: tckuhn@engr.wisc.edu

Proposed Contract Period: 12 months

Total Contract Amount: \$102,000

Indirect Cost Portion at: 15%

Table of Contents

| | |
|--|-----------|
| Research Plan..... | 1 |
| Background..... | 1 |
| Work Plan | 4 |
| Task 0 Literature Review | 4 |
| Task 1 Testing Matrix | 4 |
| Task 2 Concrete Specimen Preparation and Evaluation | 6 |
| Task 3 Data Analysis and Reporting | 7 |
| Expected Contribution from WisDOT Staff..... | 7 |
| Anticipated Research Results and Implementation Plan | 7 |
| References | 7 |
| Time Requirement | 9 |
| Budget | 10 |
| Qualifications of Research Team..... | 12 |
| Other Commitments of the Research Team..... | 12 |
| Facilities and Information Services..... | 12 |
| Laboratory Equipment | 12 |
| Certifications..... | 13 |
| Information Services..... | 13 |
| Appendix A Vita of Principal Investigators | 14 |

Research Plan

Background: Project Objective

Curing in general is known to be vital to the durability of concrete. Without proper curing cracking, scaling and a variety of maladies can be expected. It is accepted that curing can be achieved through the use of certain industrial curing compounds in contrast to other more historical and effective, but labor intensive, processes such as water ponding or wet burlap. The primary objective of curing compounds is to seal the surface so that the surface does not lose moisture (Mindess et al.¹). However as the literature shows, the actual behavior of curing compounds is not that simple. Prior research has shown that the role of curing compounds in limiting moisture loss is “not just related to better cement hydration”¹ as research has also shown curing compounds are not always effective in preventing water evaporation. Despite the perception of sealing characteristics, some curing compounds do not prevent chloride ion penetration associated with deicer application and the resulting degradation. In fact, the true role of most curing compounds is not understood other than we know they slow evaporation of water at the surface (Pigeon and Pleau²).

Improper curing can lead to three main problems, cracking, shrinkage, and scaling. It has been shown by Bentz³ and Igarishi et al.⁴ that proper curing is related to the development of the microstructure of concrete. However, this relationship is not clearly understood. Under good curing conditions, cement will hydrate with available water to produce a matrix rich in calcium silicate hydrate. With improper curing, water will leave the surface of the pavement preventing the concrete from forming the necessary hydration products responsible for the densifying the concrete structure leading to a more durable material. When the surface cement paste is depleted of water, the cement will stop hydrating and the voids will remain in the locations where water evaporated. In poorly cured concrete, hydration products are not densely packed and therefore the paste is weak. In addition, the voids allow permeation of harmful chemicals that can further deteriorate the concrete. Furthermore, without a dense paste, the structure lacks the rigidity to withstand the effects of shrinkage likely leading to cracking. Penetration of water and chlorides can also lead to scaling as the pavement endures freezing and thawing cycles. Since improper curing can lead to porous areas in the surface of the pavement, it is also reasonable to focus attention on those areas of concrete that see the highest concentrations of harmful chlorides. It is interesting to note that even when powerful deicing chemicals are used, it is curing problems that lead to more of a deterioration in the concrete than that associated with use of the deicing chemicals themselves (Van Dam et al.⁵).

Another impact of improper curing is the carbonation reaction that can occur at the surface of flatwork. Ordinary Portland cement mixtures can lose water to the atmosphere when improperly cured creating a porous matrix (Erkin⁶). These pores allow atmospheric carbon dioxide to penetrate the surface of the concrete and cause carbonation of the calcium hydroxide. Carbonation halts the hydration process leading to a weak and porous surface.

The action of curing compounds is further complicated by the introduction supplementary cementitious materials. Similar to fly ash, the use of slag cement in concrete mixtures has been linked to increased strength at later ages. However, while modest amounts of fly ash have produced highly durable concrete in Wisconsin, slag mixtures have been shown to exhibit lower resistance to freezing and thawing in the presence of deicing agents (Stark⁸, Battaglia⁹). As

concrete containing slag cures, calcium hydroxide is reduced. When this happens, calcium silicate hydrate carbonation occurs which can increase porosity and the carbonation depth that will manifest itself as a reduced resistance to scaling (Battaglia⁹ and Çopuroğlu¹⁰).

In 2005 as part of WisDOT study #0092-05-01¹¹, we examined the scaling durability of concrete in a study that closely parallels that requested by this Request for Proposals (rfp). Specifically, we examined the scaling durability of ordinary Portland cement (OPC) concrete, and 30% and 50% grade 120 slag cement concretes when subject to a variety of curing regimes including wet curing, dry curing, poly-alpha-methylstyrene curing compound, wax-based curing compound and other methods designed to limit carbonation for 60 cycles of ASTM C672 testing. Evaluations were conducted with northern igneous aggregates as well as southern limestone aggregates combined with different brands of Type I/II cement.

The work in study #0092-05-01 as reported by Battaglia et al⁹ found that curing for slag cement concrete produced essentially the opposite effect as that for OPC concrete. As shown in Fig. 1, the #0092-05-01 study with 30% substitutions of Grade 120 slag cement, established that the highest durability was achieved with the poly-alpha-methylstyrene curing compound and the lowest durability was associated with use of a wax-based curing compound. Contrary to expectations for OPC concrete, wet curing resulted in lower durability than dry curing and these findings confirmed results from several earlier unpublished investigations. This behavior that is opposite that expected of OPC has caused consternation within the concrete community and yet the literature has repeatedly shown research supporting the contrary behavior. Although it complicates the picture for concrete production, it is very clear that different cement types may warrant different curing strategies. To establish these strategies, research must not only show the impact of curing compounds on scaling but this research must also clarify the hydration mechanisms that are occurring in conjunction with the subject curing compounds.

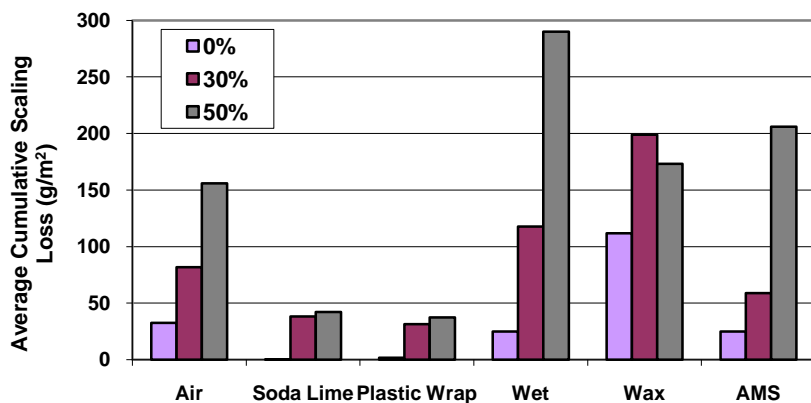


Figure 1. Average Cumulative Scaling Loss for Grade 120 Slag Cement at Replacement Levels Shown and Different Curing Regimes (AMS = poly-alpha-methylstyrene curing compound) (after LaBarca et al. ¹¹)

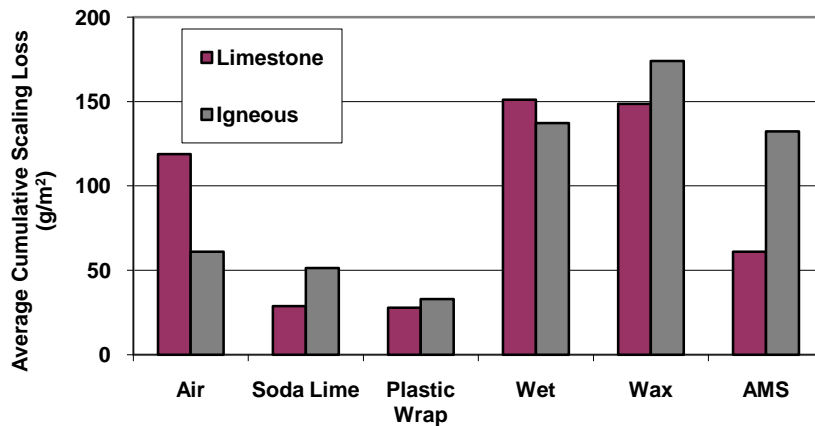


Figure 2. Average Cumulative Scaling Loss for Concrete using Wisconsin Aggregates (AMS = poly-alpha-methylstyrene curing compound) (after LaBarca et al. ¹¹).

Chloride can also play a role in the further deterioration of concrete. According to Ababneh¹², chloride penetration is due to the gradients of moisture and free chloride. Therefore, where there is ample chloride sitting atop a porous concrete slab (porosity coming from evaporation and poor curing), chloride penetration can be expected (Newald et al. ¹³). PCA¹⁴ reports: “Deicing chemicals used for snow and ice removal, such as sodium chloride, can aggravate freeze-thaw deterioration. Through osmosis, moisture tends to move towards zones having higher salt concentrations. Therefore, if salts are present in the pore solution, osmotic pressure is increased resulting in expansive pressures. In addition, the application of deicing salts to pavements increases the rate of cooling, increasing the potential for freeze-thaw deterioration at the concrete surface.”

Many studies have been conducted to determine the best practices for applying curing compounds as well as the environmental impact of such variables as wind speed and temperature on the curing process (Vandenbossche¹⁵ Kosmatka¹⁵). The Minnesota Department of Transportation (Mn/DOT) conducted a study in the late 1990’s to assess the effectiveness of curing compounds typically used in Minnesota (Vandenbossche¹⁵). In these investigation six compounds were tested: three of these compounds contained a solvent-emulsion with a resin base, two were linseed oils emulsified in water, and one was a solvent with resin base. Some compounds met Mn/DOT specifications, but still produced poor results. To remedy this poor performance, Mn/DOT developed a new requirement limiting the maximum allowable water loss to 0.15 kg/m² (0.03 lbs/ft²) in 24 hours. The standard 72-hour maximum allowable water loss was also decreased from 0.55 kg/m² (0.11 lbs/ft²) to 0.40 kg/m² (0.08 lbs/ft²). It is important to note that this study was built around the ASTM C156 procedure for determining water loss of curing compounds. Mn/DOT also now requires the use of a resin consisting of 100 percent poly-alpha-methylstyrene. Mn/DOT found that the California Department of Transportation (Caltrans) also requires the use of this resin as a curing compound because it consistently shows good water retention independent of the manufacturer. Additional results from Minnesota studies of curing compounds have shown compounds differing in chemical composition leading to different levels of effectiveness (Whitting¹⁷).

Work Plan

Our proposed research plan builds on our prior experience in the area of concrete durability. Our research will expand on previous results from study #0092-05-01 by including Grade 100 slag cement and fly ash to the extensive data base we have already gathered.

Task 0. Literature Review

Before finalizing our testing matrix, we will review the literature. The mechanisms by which curing compounds function is complex. While performance evaluations of concrete durability provide the key data for making policy decisions, the performance evaluations are only meaningful within the context of the fundamental mechanisms controlling the surface integrity of the concrete. In particular, a thorough review of the results from curing studies initiated by Minnesota as well as those of other neighboring states warrants further attention.

Task 1. Testing Matrix

Our initial testing matrix reflects that expressed in the request for proposals. As shown in Tables 1 and 2, we intend to evaluate 5 different curing compounds with respect to their effectiveness of curing concrete. In these studies we will use 2 types of Wisconsin coarse aggregate in conjunction with ordinary Portland cement, slag cement, and fly ash. The research plan includes mixing concrete to produce a sufficient number of specimens for chloride penetration and scaling tests. However, a significant portion of this investigation will be to relate the outcomes of the scaling tests to a characterization of the surface layers of the concrete specimens. This will be accomplished using carbonation tests as well as SEM and EDS analysis (described below) to identify the nature of the curing compound barrier, hydration products at the interface with this barrier, porosity of the surface region, and carbonation products.

There is one option in our proposed test matrix that warrants further discussion and research before including this in our studies. The ASTM C156 procedure for measuring water loss through the curing compound layer has been key to many of the investigations in Minnesota. To the extent possible, it would make sense to build upon the research done in Minnesota. However, our examination of this test procedure raises questions about its repeatability and effectiveness for evaluating the efficacy of curing compounds. While we have included ASTM C156 as part of a proposed testing protocol in Table 1, we would not proceed with this test until further discussion with Mn/DOT and with the Rigid Pavement TOC and thus this investigation needs to be part of Task 0 and 1. If we include this test in our matrix, we would likely need to slightly scale back effort in other areas of testing. It should be noted we have also added compressive tests to the rfp-specified list of test to provide a common baseline measure of each concrete mixture from which the durability specimens will be derived. The testing matrix would be subject to modification after consultation with the Rigid Pavement TOC.

Testing Matrix

The following testing matrix includes the tests that we anticipate conducting in this study.

Table 1: Testing Matrix

| Test | Standard | #of Tests/Batch | Timing |
|--|-----------------------|---|---|
| <i>Fresh Concrete Properties</i> | | | |
| Slump | AASHTO T119 | 1 | None |
| Air Content | AASHTO T152 | 1 | None |
| Unit Weight | AASHTO T121 | 1 | None |
| <i>Hardened Cement Properties</i> | | | |
| Compressive Strength | ASTM C39 | 3 | 28 days |
| Resistance of Concrete to Chloride Ion Penetration | AASHTO T259/ASTM 1543 | 2/period/curing regime and aggregate type | 3 and 6 months |
| Standard Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals | ASTM C672 | 3 per curing regime and aggregate type | Not less than 50 cycles (we have gone to 60 cycles in the past) |
| Standard Test Method for Water Retention by Concrete Curing Materials | ASTM 156-09a | For consideration | 72 hours |
| Carbonation | RILEM CPC18 | 5 per condition | 14, 28, 40, 60, 80 days |
| SEM carbonation and chloride penetration, and bonding of compounds | | Up to 15 analyses | 3 month, T259 samples if T259 shows sign. penetration |

Material Matrix

The following material matrix includes the materials that will be used in this study.

Table 2: Material Matrix

| Cement | | Type I or II Portland Cement | | | | | |
|------------------|--------------------------|---|-------------|-----------------|--|-------------|-----------------|
| Coarse Aggregate | | Northern source (glacial gravel) AASHTO #67 | | | Southern source (crushed limestone) AASHTO #67 | | |
| SCM | | OPC | Slag Cement | Class C Fly Ash | OPC | Slag Cement | Class C Fly Ash |
| Curing Compounds | Control | x | x | x | x | x | x |
| | Polyalphamethylstyrene | x | x | x | x | x | x |
| | Linseed oil | x | x | x | x | x | x |
| | Clear chlorinated rubber | x | x | x | x | x | x |
| | Clear acrylic | x | x | x | x | x | x |
| # of Mixes | | 5 | 5 | 5 | 5 | 5 | 5 |

Task 2. Concrete Specimen Preparation and Evaluation

Task 2.1 Collection and Characterization of the Initial Material Samples

Mix materials as listed in the rfp will be collected and characterized prior to the preparation of the concrete mixes. Aggregate will be collected from approved sources by the WisDOT. Cement, slag, and fly ash will be obtained from the recommended companies along with curing compounds.

Task 2.2 Preparation of Concrete Specimens

Concrete specimens will be manufactured as described in the rfp as shown in Table 1.

Tasks 2.3 and 2.4 Chloride and Scaling Resistance Testing

Resistance of concrete to chloride ion penetration (AASHTO T259) tests will be run on the prepared specimens. The University of Wisconsin-Madison Structures and Materials Testing Laboratory has necessary equipment to follow this procedure. The scaling test following ASTM C672 - Standard Method for Scaling Resistance of Concrete Surfaces Exposed to Deicing Chemicals will be conducted in the UW's biotron facility that provides rooms with environmentally controlled conditions. Note that we will run a modified ASTM C672 procedure that supplements the subjective visual examination with quantitative measurement of deterioration of the concrete surface due to scaling loss. These losses are typically quantified as grams per square meter as shown in Figures 1 and 2. We perfected the execution of this procedure in study #0092-05-01. As indicated above we will consider the merits of conducting ASTM 156-09a, Standard Test Method for Water Retention by Concrete Curing Materials and will run the tests if deemed important after talking to MnDOT, Nancy Whiting (now at Purdue) (Whiting¹⁷) and the Rigid Pavement TOC.

Task 2.5 SEM Analysis of Curing

A scanning electron microscope (SEM) equipped with X-ray detection (Energy Dispersive X-ray Spectroscopy or EDS) will be used to map elements (chemical compositions) that exist in the sample. The primary beam within the microscope will cause the sample to emit x-rays distinct to the existing elemental compositions. By scanning across the sample, the microscope can read what elements exist, producing an elemental map of the material. SEM analysis will be completed in the Materials Science Facility on the UW-Madison campus. EDS will be used to provide a rapid qualitative, or with adequate standards, a quantitative analysis of elemental composition with a sampling depth of 1-2 microns. X-rays will be used to form maps or line profiles, showing the elemental distribution in a sample surface. We will also explore to what extent these analysis tools will also allow us to identify how the curing compounds adhere to the surface. Using the SEM images, we expect to identify if these compounds are simply buried in pore space or if they are chemically bound to the surface altering the composition of the concrete at the site of their application. We intend to use the AASHTO T259 specimens for this analysis, however, we will down select up to 15 of the specimens most likely to produce the most meaningful results. The timeframe of this project does not allow analysis of all 30 combinations of materials. Our overriding goal is to develop an understanding at the microstructure level of the interface between the curing compound and finished concrete surface.

Task 3. Data Analysis and Reporting

Task 3.1 Data Analysis

A comprehensive data analysis will be conducted that combines the results of this study with the comparable data available from study #0092-05-01 with Grade 120 slag. Included as part of our results will be quantifiable durability measures similar to those shown in Figs. 1 and 2. In addition we intend to provide information on the bonding and surface characteristics of each curing compound.

Task 3.2 Reporting

Three quarterly reports, a closeout presentation, and a final report will be prepared for this project. TOC presentations will be made as needed or upon request.

Expected Contribution from WisDOT Staff

We expect contributions from WisDOT to be consultative in nature throughout the project. In Task 1 we expect them to contribute to determine the final testing matrix. In Task 2.1 we will incorporate their advice in selecting materials and their help in obtaining certain materials such as aggregates.

Anticipated Research Results and Implementation Plan

As demonstrable outcome, we expect to provide quantifiable results that rank the effectiveness of different curing compounds for chloride intrusion, carbonation and freeze-thaw durability for different types of concrete paving mixes. We expect to provide a description of how different curing compounds impact the surface layer of the concrete specimens. We will work with the WisDOT to implement the findings of this research. We would expect the outcome of this research combined with that of study #0092-05-01 to provide a strong basis for implementation in WisDOT guidelines and specifications. We will work directly with the Wisconsin Concrete Pavement Association to incorporate these findings into their industry recommendations.

References

1. Mindess, S., Young, J.F., Darwin, D. *Concrete*, 2nd Ed., Prentice Hall, 2003.
2. Pigeon, M. and Pleau, R. *Durability of Concrete in Cold Climates*, E & FN Spon, 1995.
3. Bentz, D. P., and P. E. Stutzman. Curing, Hydration, and Microstructure of Cement Paste. *ACI Materials Journal*, Vol. 103, No. 5, 2006, pp. 348-356.
4. Igarishi, S.; Watanabe, A.; and Kawamura, M. Effects of Curing Conditions on the Evolution of Coarse Capillary Pores in Cement Pastes. *PRO36: Proceedings of the International RILEM Symposium On Concrete Science & Engineering—A Tribute to Arnon Bentur*, K. Kovler, J. Marchand, S. Mindess, and J. Weiss, eds., RILEM Publications S.A.R.L., Paris, France, 2004.

5. Van Dam, T., K. Peterson, L. Sutter, Durability of Concrete Pavements Used for Aircraft Deicing Facilities. *Conference Proceeding Paper from Transportation Research Board 87th Annual Meeting*, 2008, pages 24.
6. Erlin, B., J. Nasvik, and L. Powers. How Much Curing is enough? *Concrete Construction - World of Concrete*, Vol. 48, No. 12, 2003, pp. 45-47.
7. Nassif, H., N. Suksawang, and M. Mohammed. Effect of Curing Methods on Early-Age and Drying Shrinkage of High-Performance Concrete. *Transportation Research Record 1834, Paper No. 03-4120*, National Research Council, 2003, pp. 48-58.
8. Stark, J., and H. Ludwig. Freeze-Thaw and Freeze-Deicing Salt Resistance of Concretes Containing Cement Rich in Granulated Blast Furnace Slag. *ACI Materials Journal*, Vol. 94, No. 1, 1997, pp. 47-55.
9. Battaglia, I., J. Munoz, and S. Cramer. Proposed Behavioral Model for Deicer Scaling Resistance of Slag Cement Concrete. *Journal of Materials in Civil Engineering*, Vol. 22, No. 4, 2010.
10. Çopuroğlu, O., A. Fraaij, A. L., and J. Bijen. Microstructural change of blast furnace slag cement paste due to carbonation. *Application of codes, design, and regulations*, University of Dundee, Scotland, 2006, pp. 229–234.
11. LaBarca, I., R. Foley, and S. Cramer. Effects of Ground Granulated Blast Furnace Slag in Portland Cement Concrete (PCP) – Expanded Study. *Wisconsin Highway Research Program #0092-05-01*, WHRP 07-01 University of Wisconsin-Madison, June 2007, pages 88.
12. Ababneh, A., and Y. Xi. An Experimental Study on the Effect of Chloride Penetration on Moisture Diffusion in Concrete. *Materials and Structures/Materiaux Et Constructions*, Vol. 35, No. 254, 2002, pp. 659-664.
13. Neuwald, A., A. Krishnan, J. Weiss, and J. Olek. Concrete Curing and its Relationship to measured scaling in Concrete Containing Fly Ash. *Submitted for Presentation to the Transportation Research Board*, Purdue University, 2002, pages 22.
14. Portland Cement Association, Durability: Freeze-Thaw Resistance. http://www.cement.org/tech/cct_dur_freeze-thaw.asp, February 19, 2010.
15. Vandenbossche, J., A Review of the Curing Compounds and Application Techniques Used by the Minnesota Department of Transportation for Concrete Pavements. *Minnesota Department of Transportation*, 1999, pages 38.
16. Kosmatka, S., and W. Panarese, Design and control of Concrete Mixtures, 13th Edition, *Portland Cement Association*, Skokie, IL, 1992.
17. Whiting, N. M., and M. B. Snyder. Effectiveness of Portland Cement Concrete Curing Compounds. *Transportation Research Record 1834, Paper No. 03-4014*, National Research Council, 2003, pp. 59-68.

Time Requirement

A tentative project schedule is shown in Table 3 for the 12 month project duration.

Table 3: Proposed Schedule

| Tasks | M1 | M2 | M3 | M4 | M5 | M6 | M7 | M8 | M9 | M10 | M11 | M12 |
|--|----|----|----|----|----|----|----|----|----|-----|-----|-----|
| T0. Literature Review | | | | | | | | | | | | |
| T1. Finalize Testing Matrix | | | | | | | | | | | | |
| T2. Concrete specimen preparation and evaluation | | | | | | | | | | | | |
| T2.1. Collection and Characterization of Materials | | | | | | | | | | | | |
| T2.2. Preparation of Concrete Specimens | | | | | | | | | | | | |
| T2.3. Chloride Testing | | | | | | | | | | | | |
| T2.4. Scaling Test | | | | | | | | | | | | |
| T2.5. SEM Analysis After Exposure | | | | | | | | | | | | |
| T3. Data Analysis and Reporting | | | | | | | | | | | | |
| T3.1. Data Analysis | | | | | | | | | | | | |
| T3.2. Reporting | | | | | | | | | | | | |

Budget

The proposed budget is \$102,000 for the 12 month duration. Research team hours and budget are show in Tables 4-6.